A THERMODYNAMIC STUDY OF ELECTROLYTIC SOLUTIONS

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1. *Scope of the investigation.*—It is well known that aqueous solutions of strong electrolytes do not conform to the requirements of the usual mass law. Measurements of freezing-point and of electric conductivity unite in showing a marked rise of the "ionization-constant" with increase of concentration. The accumulation during recent years of a considerable body of accurate data renders a theoretical examination of these relationships highly desirable.

The theory of chemical potentials, due to Willard Gibbs, offers a ready tool for examining what the rigorous consequences of the dissociation hypothesis must be. From this theory may be deduced, for example:

1°. An expression for the heat of dilution as a function of temperature and of concentration.

2°. A rigorous equation for determining the freezing-point in terms of the concentration—nothing being assumed as to the "ideal" character of the solution.

3°. A generalization of the usual mass law.

These three equations will contain certain constants, dependent on the thermic properties of the solution. Some of these constants can be calculated from specific heats, or from latent heats of melting or of evaporation. Others, in the present state of our knowledge, must be determined empirically. The constants in the three equations, in so far as they are generalizations of the usual equations, are the same. Hence any results obtained under one head can be checked by the others.

2. *Heat developed by chemical or physical changes at constant temperature and pressure.*—It is well known that when a system at constant temperature and pressure undergoes any change, the heat Q emitted during the change is connected with the total free energy φ of the system by the differential equation

$$dQ = d(T\frac{\partial \varphi}{\partial T} - \varphi) \tag{1}$$

This equation is quite general. It is not necessary that the change in question be reversible. If the system consists of several phases it is not necessary that the pressure be the same for all, provided it is constant for each.[1]

3. *The general condition of equilibrium.*—It is also well known that for a system of several phases whose composition is determined by masses m_o, m_1, m_2, ...m_n the existence of a state of equilibrium implies the equation

$$\frac{\partial \varphi}{\partial m_0} \, dm_0 + \frac{\partial \varphi}{\partial m_1} \, dm_1 + \frac{\partial \varphi}{\partial m_2} \, dm_2 + \ldots + \frac{\partial \varphi}{\partial m_n} \, dm_n = 0 \quad (2)$$

which is one of the requirements that the free energy be a minimum. The partial derivatives $\partial \varphi / \partial m_0$, etc., were called by Gibbs the chemical potentials of the respective masses. I shall denote these chemical potentials by the symbols f_0, f_1, etc., that is

$$f_0 = \frac{\partial \varphi}{\partial m_0}, \, f_1 = \frac{\partial \varphi}{\partial m_1}, \, \ldots f_n = \frac{\partial \varphi}{\partial m_n} \quad (3)$$

so that the general condition of equilibrium may be written

$$f_0 dm_0 + f_1 dm_1 + f_2 dm_2 + \ldots + f_n dm_n = 0 \quad (4)$$

Equation (4) may be said to be the kernel of the Gibbs theory.

4. *Application to the melting-point curve of ice in contact with an aqueous solution.*—Let our chemical system now consist of m_0 mols of water in which are dissolved m_1, m_2, $\ldots m_n$ mols of various solutes in contact with a mass of ice m (without subscript). If any ice melts an equal amount of water is formed, that is $dm_0 = -dm$. The masses of the solutes are unchanged, that is $dm_1 = 0$, $dm_2 = 0$, etc. Hence, equation (4) becomes for this case

$$f_0 dm_0 - f dm_0 = 0$$

that is

$$f_0 - f = 0. \quad (5)$$

When ice is in equilibrium with an aqueous solution the chemical potential of the ice is equal to the chemical potential of the solvent.

It is important to notice that f_0 is not the potential of the solvent in the pure state, but its potential as it actually exists in the solution; it is a function of the concentrations of the various dissolved substances as well as of temperature and pressure. On the other hand f, the chemical potential of the ice, is a function of temperature and pressure only. It is also important to notice that one mol of ice or water here means merely one formula-weight, and assumes nothing as to actual molecular weight. Thus the chemical potentials are the free energies per formula-weight of their respective masses.

5. *The latent heat of melting ice in contact with the solution.*—When a little water freezes out of the solution the heat emitted is determined by equation (1). The only variables are m_0 and m. We may, therefore, write

$$dQ = \frac{\partial}{\partial m_0}\left(T\frac{\partial \varphi}{\partial T} - \varphi\right)dm_0 + \frac{\partial}{\partial m}\left(T\frac{\partial \varphi}{\partial T} - \varphi\right)dm \quad (6)$$

by the ordinary formula for a total differential. But we also have, identically,

$$\frac{\partial}{\partial m_0}\frac{\partial \varphi}{\partial T} = \frac{\partial}{\partial T}\frac{\partial \varphi}{\partial m_0} = \frac{\partial f_0}{\partial T} \text{ and } \frac{\partial}{\partial m}\frac{\partial \varphi}{\partial T} = \frac{\partial f}{\partial T} \quad (7)$$

while $dm_o = -dm$, so that (6) simplifies to

$$dQ = \left[T\frac{\partial f}{\partial T} - f - T\frac{\partial f_o}{\partial T} + f_o \right] dm \tag{8}$$

We may perfectly well suppose the total amount of solution to be so great that the freezing out of 1 mol of ice does not affect its composition. The expression in brackets is then a constant. Letting Q stand for the latent heat per mol we may, therefore, write

$$Q = T\frac{\partial f}{\partial T} - f - T\frac{\partial f_o}{\partial T} + f_o \tag{9}$$

6. *The form of the melting-point equation.*—If we adopt, as a temporary notation,

$$y = f_o - f \tag{10}$$

equation (9) becomes

$$-T\frac{\partial y}{\partial T} + y = Q \tag{11}$$

whose integral is, pressure being regarded as constant,

$$\frac{y}{T} = -\int \frac{Q}{T^2} dT + F(c) + K \tag{12}$$

where $F(c)$ is a function of the concentrations of the various solutes, but not of the temperature, and K depends on neither concentrations nor temperature. Since by (5) $y = 0$ when we have equilibrium, the equation of the melting-point curve takes the form

$$-\int \frac{Q}{T^2} dT + F(c) + K = 0 \tag{13}$$

7. *The chemical potential of the solvent.*—To determine the form of the function $F(c)$ we now proceed to get an expression for the potential f_o of the water in the solution. The concentrations may be defined as

$$c_1 = \frac{m_1}{m_o}, \; c_2 = \frac{m_2}{m_o}, \; \ldots \; c_n = \frac{m_n}{m_o} \tag{14}$$

Since the potential f_o is a continuous function of the concentration and approaches φ_o the potential of the pure solvent as the solution becomes infinitely dilute, we may, as a general concept, think of f_o as expanded in a power series in the concentrations, the first term being φ_o. It is very well known, however, that, as a first approximation, the diminution of potential when any solute is added to pure water is equal to RTc, that is, as a first approximation

$$f_o = \varphi_o - RT(c_1 + c_2 + \ldots + c_n) \tag{15}$$

which holds good at infinite dilution. As a second approximation we may assume that each of the dissolved substances acts like a perfect gas, which leads to the much more accurate equation[2]

$$f_o = \varphi_o - RT\ln(1 + c_1 + c_2 + \ldots + c_n) \tag{16}$$

which holds good when the solution is "ideal." It is evident that (15) is a limiting case of (16). If, as is the main object of the present paper, we wish to investigate solutions which are not ideal, we may write the perfectly general equation

$$f_o = \varphi_o - RT\ln(1 + \Sigma c) + P(c,T) \qquad (17)$$

where Σc means the sum of the concentrations of the various solutes, and $P(c,T)$ is a power series in concentrations and temperature. This series will, for the most general expression, contain the squares, products, and higher powers of the concentrations. It will not contain the first power, for (15) must be the limiting form of the equation as the solution becomes very dilute.

Instead of the power series $P(c,T)$ explicit algebraic functions might be introduced, based either on theoretical considerations or on empirical data.[3] The main point is that some form of function in concentration and temperature must be added to the right side of (16) to obtain sufficient generality. The object of this paper is to indicate how the entrance of such a function affects the ordinary theories of freezing-point, heat of dilution, and ionization, and for this purpose the power series appears the most convenient, and can be made as general as we please by taking terms enough.

It is important to notice that equations (15), (16) and (17) all assume that we know the molecular weights of the dissolved substances, that is, Σc depends on the actual number of dissolved molecules. This is fully in accord with the usual theory of very dilute solutions. But, equally important, nothing whatever is assumed as to possible hydration of these molecules, nor as to molecular complexes occurring in the solvent. As stated above, the number of mols m_o of solvent means merely formula-weight. It is precisely such matters as hydration, polymerization of solute, and departure from gas laws which are to be taken care of by the series $P(c,T)$.

It will be most convenient to expand this series first in powers of the absolute temperature T, thus

$$P(c,T) = P_o + P_1T + P_2T^2 + \text{etc.} \qquad (18)$$

It is doubtful whether we possess any data warranting the use of powers of T higher than the square. That the square, at least, is necessary will appear. The coefficients P_o, P_1 and P_2 will be power series in the concentrations only, it being assumed that the pressure is constant. (If we vary the pressure the coefficients in these new series will vary with pressure.) The expansion (18) is, however, general enough for our present purpose. We shall, therefore, have the potential f_o of the solvent in the form

$$f_o = \varphi_o - RT\ln(1 + \Sigma c) + P_o + P_1T + P_2T^2 \qquad (19)$$

where P_o, P_1 and P_2 are functions of the concentrations, which, if ex-

panded in series, will all begin with terms of the second degree. In other words, terms in the first powers of the concentrations occur nowhere except in the logarithmic term; if it were otherwise, the solution would fail to obey the perfectly well established laws for very dilute solutions.

8. *Determination of the function $F(c)$.*—Returning now to equation (12), writing $y = f_0 - f$, and putting for f_0 its value we have

$$\frac{1}{T}(\varphi_0 + P_0 - f) + P_1 - R\ln(1 + \Sigma c) + P_2 T = -\int \frac{Q}{T^2}dT + F(c) + K \quad (20)$$

where the only terms on the left which are functions of the concentrations alone are $P_1 - R\ln(1 + \Sigma c)$. Hence, by equating,

$$F(c) = P_1 - R\ln(1 + \Sigma c) \quad (21)$$

and by using this result the equation of the melting-point curve (13) becomes

$$-\int \frac{Q}{T^2}dT + P_1 - R\ln(1 + \Sigma c) + K = 0 \quad (22)$$

where, as already stated, P_1 is a function of concentration (or of pressure if that is not constant), but not of temperature.

9. *Heat of dilution.*—Before developing (22) further, it will be well to consider in a brief way the heat of dilution emitted when 1 mol of water is mixed with a large amount of solution under the same pressure. Take the complete system as consisting of a mass of pure water M together with the solution. The potential of pure water is φ_0. By reasoning precisely as in Art. 5, and letting H stand for the heat emitted when 1 mol of water is mixed with a large amount of solution,

$$H = T\frac{\partial f_0}{\partial T} - f_0 - T\frac{\partial \varphi_0}{\partial T} + \varphi_0 \quad (23)$$

Introducing the value of f_0 from (19) this becomes

$$H = P_0 - + P_2 T^2 \quad (24)$$

The absence of the term in the first power of T is noticeable.

If the heat of dilution at constant pressure be expanded in powers of T, the first power is rigorously absent.

9. *The equation of the melting-point curve.*—Returning now to (22), we may think of the heat of melting Q as composed of two parts, first the heat of melting at that temperature in contact with pure water, second the heat of dilution. The first we may call Q_0, the second is $-H$ (since Q was taken as heat emitted on freezing). Thus

$$Q = Q_0 - H \quad (25)$$

Without assuming the results of the last article, we may expand H in powers of T,

$$H = H_0 + H_1 T + H_2 T^2 \quad (26)$$

It is more convenient to expand Q_0 in powers of t, where $t = 0$ is the freezing-point of pure solvent,

$$Q_0 = q + q't \qquad (27)$$

so that q is the latent heat of freezing per mol in contact with pure solvent, while q', to a good approximation, is the difference of specific heats of solvent in liquid and solid state. It is not likely that a term in t^2 will be needed with our present data, but can be introduced if wanted. It is important to notice that q and q' are not functions of concentration, by definition. Inserting values of H and Q_0 on the right side of the identity (20) and performing the integration we have (putting $t = T - T_0$),

$$\frac{1}{T}(\varphi_0 + P_0 - f) + P_1 - R\ln(1 + \Sigma c) + P_2 T = \frac{q - q'T_0}{T} - \frac{H_0}{T} +$$
$$H_1 \ln T + H_2 T + P_1 - R\ln(1 + \Sigma c) + K - q'\ln T; \qquad (28)$$

Comparing like terms on the two sides of this identity, we see that on the left the only term involving T^{-1} and varying with concentration is P_0/T while on the right the only like term is $-H_0/T$, hence $H_0 = -P_0$. Again, on the left there is no term in $\ln T$ varying with concentration, hence $H_1 = 0$. Terms in T give $H_2 = P_2$. Thus

$$H = -P_0 + P_2 T^2$$

which checks with (24). Collecting results, and substituting in (22) we have the equation of the melting-point curve as

$$\frac{q - q'T_0}{T} + \frac{P_0}{T} + P_2 T - R\ln(1 + \Sigma c) + K + P_1 - q'\ln T = 0 \quad (29)$$

where the constant K is yet undetermined. When $T = T_0$ the quantities P_0, P_1 and P_2 are zero since the concentration is zero. This gives for K

$$K = \frac{q}{T_0} + q' + q'\ln T \qquad (30)$$

whence the melting-point equation by a little arrangement is

$$RT\ln(1 + \Sigma c) - P(c,T) = q\left[1 - \frac{T}{T_0}\right] - q'(T - T_0) - q'T\ln\frac{T}{T_0} (31)$$

10. *Discussion of the melting point equation.*—Equation (31) departs from strict generality only in so far as we have failed to expand to higher powers of T. In principle it is entirely rigorous, and whenever we have data to warrant it we may expand as far as we please. It shows that a rigorous theory differs from the ordinary theory only through the function $P(c,T)$ which, if expanded in powers of the concentrations, begins with terms of the second degree, but which, if expanded in powers of T, contains a term $P_1 T$ playing no part in heat of dilution. To omit $P(c,T)$ altogether is, therefore, equivalent to something more than assuming heat of dilution to be zero.

If $P(c,T)$ be dropped, the equation becomes identical (except for slight difference of notation) with the melting-point equation established in a valuable paper by Washburn[4] on the two hypotheses:

1°. That the vapor of the solvent acts like a perfect gas.

2°. That Raoult's law holds good for the lowering of vapor pressure.

Since our equation (31) has been obtained without any recourse to vapor pressure, we may at once follow Washburn's reasoning in inverse order and get a certain amount of new light on the two assumptions about vapor pressure. For by differentiating (13) with respect to T we have

$$\frac{Q}{T_2} = F'(c)\frac{dc}{dT} \tag{32}$$

supposing there is only one dissolved substance. Using $F'(c)$ from (21) we have

$$\frac{Q}{T^2} = \left(P'_1 - \frac{R}{1+c}\right)\frac{dc}{dT} \tag{33}$$

which aside from slight difference of notation, differs from Washburn's differential equation in the presence of P'_1, which we have seen to be a function of c. Taking then the rigorous equation[5]

$$\frac{Q}{vT} = \left[\frac{\partial p}{\partial c}\right]_T \frac{dc}{dT} \tag{34}$$

where p is the vapor pressure, and eliminating dc/dT

$$\left[\frac{\partial p}{\partial c}\right]_T = \left(P'_1 - \frac{R}{1+c}\right)\frac{T}{v} \tag{35}$$

So far we have made no assumptions. If we assume $pv = RT$ we have by integrating

$$p_0 = p(1+c)e^{P_1} \tag{36}$$

a generalization of Raoult's law, to which it reduces if $P_1 = 0$. It is noteworthy that P_1 is the coefficient of precisely the term in the expansion of $P(c,T)$ which does not affect the heat of dilution. In other words the departure of the vapor from Raoult's law is dependent on the function $P(c,T)$, which affects the freezing-point, *minus* all the terms which affect the heat of dilution. Thus if heat of dilution and freezing-point are known we can find the vapor pressure, a fact also pointed out by Washburn. Equation (36) shows the precise relation of this fact to the melting-point equation provided we assume $pv = RT$. In any case (35) shows that the vapor pressure of a solution can be calculated if we know the coefficient of T in the chemical potential of the solvent, and the equation of state the vapor.

It will now be apparent that we can determine empirically the coefficients in the expansion of $P(c,T)$ and hence have a complete knowledge of the properties of the solution if we can get accurate determinations of heat of dilution at various temperature and over a considerable range of

concentrations, and also have accurate freezing-point determinations at fairly high concentrations, so as to calculate the missing term P_1. It is doubtful if any such data of high accuracy now exist over a wide enough range for even one substance. If, however, the accurate methods which have been used[6] to obtain freezing-point data for very dilute solutions can be carried to higher concentrations, and if the accurate data on heat of dilution[7] which have been obtained at 25° can be carried over a moderate temperature range, there seems to be no doubt we should have a theory of solution that would be practically complete. A detailed examination of existing data in the light of the foregoing theory is now under way, but would too greatly lengthen the present paper. A single example must here suffice. Taking cane sugar, and, as a first approximation, considering only terms in the square of the concentration, i.e., dropping the cube and higher powers in the expansion of $P(c,T)$ the coefficient C_2 of this term was calculated for values of N, the number of mols sugar per 1000 grams of water. The data[8] of Morse and Fraser gave

N............	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2681
C_2............	0.110	0.122	0.098	0.119	0.119	0.118	0.121	0.133	0.115

while the data[9] of Ewan gave

N............	0.8714	1.2908	1.5347	1.6427	2.1108
C_2............	0.118	0.104	0.132	0.128	0.132

Raoult's data[10] gave:

N..........	0.5056	1.0107
C_2..........	0.117	0.124

Other data quoted by Landolt and Bernstein gave

N............	0.760	0.4236	0.2840
C_2............	0.061	0.094	0.097

It is evident that the values of C_2 from the data of these different observers do not agree well. Below about 0.3 normal the solution departs so little from the "ideal" that the calculations become meaningless, depending as they do on differences between ideal and observed numbers.

11. *Application of the foregoing theory to electrolytes.*—Let us now suppose that the only dissolved substance is a single uni-univalent salt, as KCl. Calling c the formal concentration per 1000 grams of water we shall have

$$m_o = 55.5, m_1 = m_2 = c\gamma, \text{ and } m_3 = c(1 - \gamma)$$

where γ is the fraction of salt which is ionized, m_1 and m_2 the masses of the ions in mols, and m_3 the mols of un-ionized salt. At a given temperature $P(c,T)$ becomes a function of c alone and we may write

$$P(c) = Ac^2\gamma^2 + Bc^2\gamma(1 - \gamma) + Cc^2(1 - \gamma)^2 + \ldots \quad (37)$$

where $A, B, C, \ldots$ are constants to be found. It is evident from the form of these terms that they will be without influence in very dilute solution,

hence ionization as calculated from freezing-point by the ordinary formula should be exact.

12. *Generalization of the mass law.*—The case is quite otherwise, however, when we consider equilibrium between the ions and un-ionized salt. For if we let f_1 and f_2 denote the chemical potentials of the ions, f_3 that of the un-ionized salt, the general condition (4) of equilibrium gives

$$f_1 + f_2 = f_3 \tag{38}$$

as the equation which determines the ionization. Now by definition

$$f_0 = \frac{\partial \varphi}{\partial m_0}, \; f_1 = \frac{\partial \varphi}{\varphi m_1}, \; f_2 = \frac{\partial \varphi}{\partial m_2} \text{ and } f_3 = \frac{\partial \varphi}{\partial m_4}$$

and if T be regarded as constant we may expand $P(c,T)$ in the form

$$P(c) = \frac{1}{m_0^2}[a_{11}m_1^2 + a_{12}m_1m_2 + \text{etc.}] + \frac{1}{m_0^3}[a_{111}m_1^3 + a_{112}m_1^2m_2 + \text{etc.}], \tag{39}$$

while, from (17), f_0 can be written

$$f_0 = \varphi_0 - RT \ln (m_0 + m_1 + m_2 + m_3) + RT \ln m_0 + P(c) \tag{40}$$

Taking the derivative with respect to m_1,

$$\frac{\partial f_0}{\partial m_1} = -\frac{RT}{m_0 + m_1 + m_2 + m_3} + \frac{1}{m_0^2}[2a_{11}m_1 + a_{12}m_2 + a_{13}m_3]$$

$$+ \frac{1}{m_0^3}[3a_{111}m_1^2 + 2a_{112}m_1m_2 + 2a_{113}m_1m_3 + a_{122}m_2^2 + a_{123}m_2m_3 + a_{133}m_3^2]$$

Now we have identically

$$\frac{\partial f_0}{\partial m_1} = \frac{\partial^2 \varphi}{\partial m_0 \partial m_1} = \frac{\partial f_1}{\partial m_0}$$

whence $f_1 = \int \frac{\partial f_0}{\partial m_1} dm_0 +$ terms not involving m_0. Therefore,

$$f_1 = \varphi_1 + RT\ln\left[\frac{m_1}{m_0 + m_1 + m_2 + m_3}\right]$$

$$- \frac{1}{m_0}[2a_{11}m_1 + a_{12}m_2 + a_{13}m_3] - \frac{1}{2m_0^2}[3a_{111}m_1^2, \text{etc.}]$$

where φ_1 involves temperature (and pressure) only. The presence of the term $RT \ln m_1$ is determined from our hypothesis that the solution acts like a perfect gas to a first approximation.[11] It is noteworthy that terms in f_0 involving *squares* of concentrations lead, in f_1, to terms of the *first* degree. Expressions for f_2 and f_3 are similarly found. If we put

$$x_1 = \frac{m_1}{m_0 + m_1 + m_2 + m_3}$$

with similar notation for x_2 and x_3, and substitute in (38) the expressions for f_1, f_2 and f_3 we shall have as the condition of equilibrium

$$\ln\left[\frac{x_1 x_2}{x_3}\right] - G(c) = k \qquad (41)$$

where $G(c)$ is a function of concentration, which, if expanded in series, begins with terms of the first degree in the masses of the dissolved substances. The coefficients in the expansion are functions of temperature (and pressure), and k is also a function of temperature. If we omit $P(c,T)$ in f_0 we must also omit $G(c)$ in this extended mass law (41). It is noteworthy that in the logarithmic term we have rigorously x_1, x_2, x_3, not m_1/m_0, etc., although in solutions not very concentrated it does not matter much.

13. *Discussion of the generalised mass law.*—It is shown in the foregoing theory that if the function $P(c,T)$ can be accurately determined we can at once calculate the function $G(c)$ and hence predict to what extent ionization departs from the mass law. This could be done from accurate measurement of heat of dilution, checked as to terms in T by freezing-point data. Conversely, if ionization be known, we can find $G(c)$ and hence $P(c)$ for that temperature. Many other relations can be brought to bear particularly those connecting specific heats with change in equilibrium under varying temperature.

Furthermore equation (41) can be employed to study the theoretical form of the curve obtained by plotting the "constant" K against the formal concentration c. By putting $m_1 = m_2 = c\gamma$ and $m_3 = c(1 - \gamma)$ we may write (41) as

$$K = \frac{\gamma^2 c}{1 - \gamma} = K_0 e^g \qquad (42)$$

where g is a function of concentrations which may be expanded

$$g = ac\gamma + a'c(1 - \gamma) + \text{etc.} \qquad (43)$$

By differentiating with respect to c we have

$$\frac{dK}{dc} = K_0 e^g \frac{dg}{dc} \qquad (44)$$

while dg/dc found from (43) is

$$\frac{dg}{dc} = a\gamma + a'(1 - \gamma) + (a - a')c\frac{d\gamma}{dc} \qquad (45)$$

and the value of $d\gamma/dc$ from (42) is

$$\frac{d\gamma}{dc} = \frac{[ac\gamma + a'c(1 - \gamma) - 1]\gamma(1 - \gamma)}{c[2 - \gamma + c\gamma(1 - \gamma)(a' - a)]} \qquad (46)$$

Now as c approaches zero, γ approaches unity. By inspection of (46) we see that $cd\gamma/dc$ approaches zero, for the denominator approaches unity on cancelling c. Hence from (45) we see that dg/dc approaches the constant a. Hence by (44) we have

$$\text{Lim } \frac{dK}{dc} = aK_o \tag{47}$$

This means that we shall not naturally expect the electrolyte to obey the mass law even in very dilute solution. For this would, in strict rigor, mean that the graph of K against c should have a horizontal tangent as c approaches zero. However, a curve differing little from the horizontal would be hard to distinguish experimentally from the other.

In a highly interesting investigation Washburn has worked out this curve for KCl at extreme dilutions,[12] assuming that the graph of K shows no marked change in character as c approaches zero. To compare his results with the present theory I have assumed that his value of Λ_o is correct and also his value 0.02 for K_o. Determining the function g so that the following data (from Washburn and from Adams) should be exactly satisfied:

c............	0.0004	0.001	0.005
γ............	0.98923	0.98163	0.958

the function g was found to satisfy

$$g \log_{10} e = 1075c\gamma - 47234c(1 - \gamma) + 240064c^2\gamma^2$$

Values of γ calculated from this equation were then compared with Washburn's results for round concentrations:

c............	0.00005	0.0001	0.0002	0.0003	0.0007	
γ............	0.99796	0.99595	0.9931	0.9910	0.98507	(Calc.)
γ............	0.99753	0.99529	0.99256	0.99083	0.98511	(Washburn)

The curve for K plotted from the calculated values of γ lies very slightly higher than Washburn's curve at concentrations below 0.0004, but approaches 0.02 as c approaches zero. It coincides almost exactly with Washburn's curve above 0.0004 differing from his curve in having but slight inflection. An inspection of his diagram makes it clear that a curve meeting the vertical axis at a small angle with the horizontal, and having but little inflection still fits his data very well, and, of course, would fit entirely with his supposition that no marked change occurs in the character of the curve at infinite dilution. It is highly probable, too, that the empirical value of g given above is not the best that can be found. Further investigation is now being conducted.

14. *Summary.*—The adoption of Gibbs' principle of chemical potentials leads to an extention of the ordinary theories of melting-point, heat of dilution, vapor pressure, and mass law. In all cases these extensions are the result of the presence, in the expression for the chemical potential of the solvent, of terms in the square and higher powers of the concentrations. In many phenomena these terms are without measurable effect in dilute solution. They lead in the case of the mass law to terms in the first

power of the concentrations, hence are important even in very dilute solutions.

[1] Duhem, *Méchanique Chimique*, Livre VI, Chap. 111.   The function $T\partial\varphi/\partial T - \varphi$ is identically equal to Gibbs' heat function $U + pv$.

[2] *Ibid.*

[3] Van Laar, *Sechs Vortrage u. d. thermodynamische Potential*, S. 84.

[4] *Technology Quart.*, Boston, **21**, 1908 (372).

[5] *Ibid.*, p. 371.

[6] Adams, L. H., *J. Amer. Chem. Soc.*, **37**, 1915 (481).

[7] MacInnes and Braham, *Ibid.*, **39**, 1917 (2110).

[8] *Amer. Chem. Jour.*, **34**, 1905; **37, 38**, 1907.

[9] *Zs. phys. Chem.*, **31**, 1899; and **27**, 1898.

[10] Duhem, *loc. cit.*

[11] These PROCEEDINGS, **3**, 1917 (569); see also *J. Amer. Chem. Soc.*, **40**, 1918 (106–158).

[12] These PROCEEDINGS, **3**, 1917 (574) and *J. Amer. Chem. Soc.*, **40**, 1918 (145).

THE FORMATION OF THE CELL PLATE IN THE CAMBIUM OF THE HIGHER PLANTS

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In a previous note[1] the writer called attention to a remarkable type of cytokinesis that occurs in the cambium of Coniferae. The process of cell plate formation is greatly extended, both as regards space and time and is clearly dissociated, except in its initial stages, from·the usual phenomena of karyokinesis. Since this type of cell division promises to be of considerable significance in the study of various cytological and physiological problems[2] it is desirable to determine whether it is an isolated phenomenon, i.e., confined to the Coniferae, or one that is characteristic of the cambia of all of the higher plants, angiosperms as well as gymnosperms.

During the last growing season, I secured specimens of the cambium from an extensive series of angiosperms. Selections were made so as to include representatives of all of the larger and more important orders of the dicotyledons and of certain arborescent monocotyledons which have "secondary" growth in thickness. Specimens were obtained from both tropical and temperate environments.

Although the cambial initials in mature stems of angiosperms are on an average considerably smaller than homologous elements of gymnosperms[3] the salient features of cytokinesis are the same in both subphyla. In the former, as in the latter group, each initial contains a single nucleus which is centrally located and divides mitotically. The spindle becomes extended laterally by the addition of peripheral "fibers"[4] and gradually assumes the form of a disk, figures A and B. As more fibers are successively added the original "connecting fibers" disappear from about the cell